Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry

1 Location

1.1 All sample peparation and testing occurs in the spectroscopy laboratory, room 305.

2 Purpose

2.1 The purpose of this method is to provide instructions for the determination of trace metal constituents in water and waste samples.

3 Applicability

3.1 This method provides procedures for the determination of dissolved elements in ground waters, surface waters and drinking water. it may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and soils samples. This method is applicable to the following elements:Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Thallium, Thorium, Uranium, Vanadium and Zinc.

3.2 Estimated instrument detection limits (IDLS) for these elements are listed in Table 1. However, actual method detection limits (MDLS) and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions. Given in Table 2 are typical MDLs and reporting levels for both total recoverable determinations by direct analysis and where sample digestion is employed.

Table 1: Calculated Instrument Detection Levels

Analyte	Mass	IDL
Beryllium	9	0.36
Vanadium	51	0.071
Chromium	52	0.12
Cobalt	59	0.027
Nickel	60	0.18
Copper	63	0.14
Zinc	66	0.14
Arsenic	75	0.26
Selenium	82	0.84
Molybdenum	98	0.06
Silver	107	0.37
Cadmium	111	0.020
Antimony	123	0.038
Barium	137	0.079
Thallium	205	0.016
Lead	206 + 207 + 208	0.035
Thorium	232	0.27
Uranium	238	0.023

Table 2: Calculated Method Detection Levels

Analyte	Mass	MDL	Reporting
Beryllium	9	0.1	1.0
Vanadium	51	0.1	1.0
Chromium	52	0.1	1.0
Cobalt	59	0.02	1.0
Nickel	60	0.05	1.0
Copper	63	0.1	1.0
Zinc	66	0.2	1.0
Arsenic	75	0.2	1.0
Selenium	82	0.2	1.0
Molybdenum	98	0.05	1.0
Silver	107	0.03	1.0
Cadmium	111	0.04	1.0
Antimony	123	0.1	1.0
Barium	137	0.03	1.0
Thallium	205	0.03	1.0
Lead	206 + 207 + 208	0.05	1.0
Thorium	232	0.2	1.0
Uranium	238	0.02	1.0

3.3 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

3.4 Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.1% w/v (approximately 3000 µmhos/cm conductivity).

3.5 Where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the samples have been properly preserved with acid and have turbidity of < 1 NTU at the time of analysis. This total recoverable determination procedure is referred to as “direct analysis”.

3.6 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils. sludges., sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample.

3.7 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended.

3.8 Users of this method must document and have on file the required initial demonstration of performance as described in section 9.2 of Method 200.8, revision 5.4 of the US EPA prior to using the method for analysis.

4 Scope

4.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric acid. After cooling, the sample is filtered to remove large particulate and made up to volume (Method I-1-32). For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is < 1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid.

4.2 The method describes the multi-element determination of trace elements by ICP-MS. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier detector and the ion

information processed by a data handling system. Interferences relating to the technique must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards.

5 Definitions

5.1 Calibration Blank - A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

5.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

5.3 Dissolved analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter assembly prior to sample acidification.

5.4 Field Reagent Blank (FRB) - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

5.5 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the selected analytical mass(es).

5.6 Internal Standard - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

5.7 Laboratory Duplicates (LD1 and LD2) - Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

5.8 Laboratory Fortified Blank (LFB) - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

5.9 Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

5.10 Laboratory Reagent Blank (LRB) - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

5.11 Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

5.12 Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.

5.13 Quality Control Sample (QCS) - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.

5.14 Solid Sample - for the purpose of this method, a sample taken from material classified as either soil, sediment, sludge or fish tissue.

5.15 Stock Standard Solution - A concentrated solution containing one or more method analytes prepared , in the laboratory using assayed reference materials or purchased from a reputable commercial source.

5.16 Total Recoverable Analyte - The concentration of analyte determined either by

direct analysis of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU, or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in method I-1-32.

5.17 Tuning Solution - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

5.18 Water Sample - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

6 References

6.1 Long, S. E. And Martin, T. D. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma Mass Spectrometry Revision 5.4. Methods for the Determination of Metals in Environmental Samples. Supplement I. EPA 600/R-94/111, May 1994. PB95-125472. Method 200.8.

6.2 Perkin Elmer/SCIEX. Users Manual, ELAN 5000, Inductively coupled plasma mass spectrometry.

7 Discussion

7.1 Interferences: Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

7.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. It should be noted that such corrections will only be as

accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations.

7.1.2 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

7.1.3 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same-nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample componenents. Most of the common interferences have been identified and these are listed in Table 2 of Method 200.8, revision 5.4 of the USEPA together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common ^{82}Kr interference that affects the determination of both arsenic and selenium, can be greatly reduced with the use of high purity krypton free argon.

7.1.4 Physical interferences - Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.1% (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical

interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

7.1.5 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the method detection limit, should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period. In the determination of mercury, which suffers from severe memory effects, the addition of 100 µg/L gold will effectively rinse 5 µg/L mercury in approximately 2 minutes. Higher concentrations will require a longer rinse time.

7.2 Safety

7.2.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analysis. Specifically, concentrated nitric -and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always, wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

7.2.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

7.2.3 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV emissions.

8 Sample Handling and Preservation

8.1 If properly acid preserved, the sample can be held up to 6 months before analysis.

8.2 For the determination of dissolved elements, the sample must be filtered through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Use a portion of the sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with nitric acid immediately following filtration to pH < 2.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH < 2 (normally, 2 mL of nitric acid per 200 mL, 4 mL of nitric acid per 1000 mL of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination the samples may be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior to withdrawing an aliquot for processing or "direct analysis" if for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2. When the nature of the sample is either unknown or known to be hazardous, acidification should be done in a fume hood.

8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

9 Apparatus and Materials

9.1 Perkin Elmer/Sciex ELAN 5000 Inductively Coupled Plasma Mass Spectrometer

9.2 Variable speed 4 channel peristaltic pump

9.3 4 channel mass flow controller for control of argon gasses

9.4 40 MHz free running radio frequency generator

9.5 Argon, High purity grade (99.99%). Use only from "gas pack" dewars supplied by local gas distributer.

9.6 Eppendorf pipetter, 200-1000 µL range

9.7 Eppendorf pipettor, 10-100 µL range

9.8 Labware - For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory -apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 10% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with reagent grade water and storing clean. Chromic acid must not be used for cleaning glassware.

9.8.1 Glassware - Volumetric flasks, Class A Glass

9.8.2 Assorted Class A pipets

9.8.3 Storage bottles, Nalgene, Various sizes.

9.8.4 Wash bottle with screw cap closure

9.9 Reagents and Standards

9.9.1 Nitric Acid, concentrated Instrumental grade.

9.9.2 Hydrochloric Acid, concentrated Instrumental grade

9.9.3 Reagent water. All references to reagent grade water in this method refer to ASTM type I water (ASTM D1193).

9.9.4 Standard Stock Solutions. Purchase standards at a level of 1000 mg/L from a reputable source. Replace yearly.

9.9.5 Multielement Stock Standard Solutions. Care must be taken in the preparation of multielement stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities-which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, not previously used LDPE Nalgene bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

9.9.5.1 Standard Solution A: 1 mg/L each of Aluminum, Antimony, Arsenic, Beryllium, Cadmium, Chromium, Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Thallium, Thorium, Uranium and Vanadium.

9.9.5.2 Standard Solution B: 1 mg/L each of Barium, Silver and Zinc.

9.9.5.3 Multielement stock standard solutions A and B may be prepared by diluting 0.1 mL of each single element stock standard in the combination list to 100 mL with reagent water containing 1% (v/v) nitric acid. Replace the multielement stock standards when succeeding dilutions for preparation of the calibration standards cannot be verified with the quality control sample. Solution B may be prepared gravimetrically directly into 125 mL plastic storage bottles if glassware contributes to zinc contamination.

9.9.5.4 For Lead and Copper samples prepare a series of standards by diluting directly from the stock standards. The standards should have levels of copper and lead respectively (units in µg/L): pbcu#3: 500,25; pbcu#2: 1000,50; pbcu#1A: 3000,100. Replace every month or as needed.

9.9.5.5 For the full trace element suite fresh multielement calibration standards should be prepared every month or as needed. Dilute each of the stock multielement standard solutions A and B to levels

of 2 µg/L, 10 µg/L, 50µg/L and 200µg/L (with the exception of mercury) using reagent water containing 1% v/v) nitric acid. Calibration standards should be verified initially using a quality control sample. 500 ug/L and 1000 ug/L concentrations may also be used as appropriate.

9.9.6 Internal standards are added through a separate channel on the peristaltic pump. Depending on what is being tested, prepare the appropriate internal standard as follows.

9.9.6.1 For Lead and Copper testing dilute 0.1 mL of 1000 mg/L Bismuth and 0.1 mL of 10000 mg/L Scandium to a volume of 1000 mL. This will contain 1000 µg/L Scandium and 100 µg/L Bismuth.

9.9.6.2 For the full suite of elements dilute 0.1 mL of 1000 mg/L solution of depleted ^{6}Lithium and 0.1 mL each of 1000 mg/L solutions of Scandium, Rhodium and Bismuth. Also add 0.2 mL of 1000 mg/L gold to aid in washout of mercury. This solution will contain 100 µg/L ^{6}Lithium, Scandium, Rhodium and Bismuth and 200 µg/L Gold.

9.9.7 Blanks - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

9.9.7.1 Calibration blank - Consists of 1% (v/v) nitric acid in reagent grade water.

9.9.7.2 Laboratory reagent blank (LRB) -Must contain all the reagents in the same volumes as used in processing the samples.. The LRB must be carried through the same-entire preparation scheme as the samples including digestion, when applicable.

9.9.7.3 Rinse blank - Consists of 2% (v/v) nitric acid in reagent grade water.

9.9.8 Tuning Solution - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, rhodium, lead, barium and cerium stock solutions

in 1% (v/v) nitric acid to produce a concentration of 10 µg/L of each element.

9.9.9 Quality Control Sample (QCS) - The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS dilute an appropriate aliquot of analytes to a concentration ≤ 100 µg/L in 1% (v/v) nitric acid. Because of lower sensitivity, selenium may be diluted to a concentration of < 500 µg/L, however, in all cases, mercury should be limited to a concentration of ≤ 5 µg/L. The QCS should be analyzed as needed to meet data-quality needs and a fresh solution should be prepared quarterly or more frequently as needed

9.9.10 Laboratory Fortified Blank (LFB) - To an aliquot of LRB, add aliquots from multielement stock standards A and B to prepare the LFB. Depending on the sensitivity of the instrument, the fortified concentration used should range from 40 µg/L to 100 µg/L for each analyte. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

10 Procedures

10.1 Daily Warmup

10.1.1 Vacuum stays on at all times. If vacuum happened to fail, start it and allow it at least 30 minutes to come to a stable vacuum pressure.

10.1.2 If running lead and copper and pump tubing is worn replace the pump tubing on the peristaltic pump daily. If running the full suite of trace metals and zinc is requested on the samples being run, use peristaltic pump tubing that has been "broken in". This would be tubing which has been on the pump with 1% nitric acid/water solution or samples being pumped through it for approximately 3-4 hours. Failure to follow this precaution will lead to elevated levels of zinc in the blank and zero standard.

10.1.3 Examine the sampler and skimmer cones. If they appear blocked or many samples have been run since they were cleaned, remove this set and replace with cleaned backup set. Then clean the removed set.

10.1.4 Aspirate water through both the internal standard tubing and the

autosampler probe tubing.

10.1.5 Ignite the plasma. This involves pressing the yellow switch on the front of the instrument labeled plasma on/off.

10.2 Create a list of samples to run

10.2.1 While the instrument is warming up, create a sample queue. This involves logging into the lims and creating either a icpms2 worklist for lead and copper only, or an icpms20 or icppms20d worklist for the full suite of trace metals or dissolved trace metals respectively.

10.2.2 Fill the autosampler tray with samples, standards, and quality control samples and place it on the autosampler.

10.2.3 At this time you may choose to set up the data set file which contains the sample identification for the samples which you will be running.

10.2.3.1 In the application software choose applications-quantitative.

10.2.3.2 Choose open data set file

10.2.3.3 Type in a name following the convention yymmdd.?%. Replace the ? in this example with either pbcu for lead copper samples and the % with a number indicating which set this is of that type for the day. For example on 12-22-95 you choose to run one full suite of metals. The data set file will be named 951222.trace1.

10.2.3.4 For lead and copper samples the sequence of samples to use is as follows:

Sample ID	Sample Type
Blank	blank
pbcu#4	standard (0)
pbcu#3	standard (25,500)
pbcu#2	standard (50,1000)
pbcu#1	standard (100,3000)
check (both QCS & LFB for first set of the day)	qc check (LFB)

Sample ID	Sample Type
lims log number (10/set)	sample
spike	qc spike
duplicate	qc duplicate
check	qc check (LFB)
bsln_chk	qc check of baseline

10.2.3.5 For trace metals the sequence of samples to use is:

Sample ID	Sample Type
Blank	blank
mixab_0	standard (0)
mixa_2	standard (2 most metals)
mixb_2	standard (2 Ba, Ag, Zn)
mixa_10	standard (10 most metals)
mixb_10	standard (10 Ba, Ag, Zn)
mixa_10	standard (10 most metals)
mixb_10	standard (10 Ba, Ag, Zn)
mixa_50	standard (50 most metals)
mixb_50	standard (50 Ba, Ag, Zn)
mixa_200	standard (200 most metals)
mixb_200	standard (200 Ba, Ag)
check (both LFB and QCS for first set of the day)	qc check (LFB)
lims log number (10/set)	sample
spike	qc spike
duplicate	qc duplicate

check	qc check (LFB)
bsln_chk	qc check of baseline

10.2.3.6 You may choose to use the software tools of cut and paste (from previous data sets) or set defaults to aid in filling the sample queue. Refer to the users manual for instructions on using these features.

10.2.3.7 Identify the correct autosampler position numbers for all samples and standards.

10.2.3.8 Identify the correct sample type for all samples and standards.

10.2.3.9 Open up the proper parameter set. For lead and copper it is pbcu and for the trace metals it is 200.8_5.4.

10.2.3.10 Select summary as the report type (Reports-summary).

10.2.3.11 Clear the Data Set Summary (options-clear data set summary).

10.2.3.12 Clear any stored calibration (calibration-clear calibration).

10.2.3.13 If you have already tuned the instrument (bypassed 10.2.3 initially and came back to it) go to starting the analysis (sec 10.5).

10.3 Tune the instrument.

10.3.1 Optimize the mass calibration curve.

10.3.1.1 Aspirate the tuning solution.

10.3.1.2 Load the graphics application.

10.3.1.3 Open the setup data set.

10.3.1.4 Open the setupnew parameter set.

10.3.1.5 Make sure reporting is turned off (Reports-no checks by either summary or comprehensive).

10.3.1.6 Make sure numeric view is selected (View-Numeric).

10.3.1.7 Run the tuning solution as a sample.

10.3.1.8 While sample results are displayed on screen, optimize for high counts on rhodium and oxides less than 3%. This involves optimization of: torch sampling depth, nebulizer flow rate, plasma power, ion lenses. For detailed instructions on this procedure see the users manual.

10.3.1.9 Equalize counts on lead and magnesium while maintaining optimized rhodium counts and oxides less than 3%. This involves tuning of the ion lenses. Again, see the users

manual for detailed instructions.

10.3.1.10 Record all relevant data in the ICPMS Maintenance/Tuning book.

10.3.2 Check oxide and double charged levels.

10.3.2.1 Aspirate the tuning solution.

10.3.2.2 Open the oxides data set.

10.3.2.3 Open the oxides parameter set.

10.3.2.4 Run the tuning solution.

10.3.2.5 If oxides or doubly charged ions are greater than 3% relative—CeO to Ce, Ba++ to Ba—, return to step 10.3 and retune.

10.3.2.6 Record doubly charged and oxide levels in the ICPMS Maintenance/Tuning book.

10.3.3 Optional: Check baseline.

10.3.3.1 Aspirate deionized water with internal standard probe, 1% nitric acid with autosampler probe.

10.3.3.2 Open the baseline data set.

10.3.3.3 Open the baseline parameter set.

10.3.3.4 Turn reporting on (Reports-Comprehensive).

10.3.3.5 Run the solutions described in 10.3.3, 10.3.3.1.

10.3.3.6 Compare the run of the baseline with the previous setups run and store these results in the baseline book.

10.4 If not done previously, set up an analysis queue as in sec 10.2.

10.5 Analyze the samples.

10.5.1 If not already there, go to the quantitative analysis application (applications-quantitative).

10.5.1.1 Open the data set which you want to run.

10.5.1.2 Load the parameters which you will be using to analyze the samples.

10.5.2 If you will be running into the night shut torch off after aquisition (Analyze-shut off torch).

10.5.3 Make sure all samples and standards are in the autosampler and ready to go.

10.5.4 Insert the internal standard probe into the internal standard flask. Allow the internal standard to reach the torch interface.

10.5.5 Start the analysis. Typically you will want to analyze the samples to the end of the run. Press shift-f12.

10.6 Evaluate the results.

10.6.1 Periodically examine the reports.

10.6.1.1 The internal standard should drift no more than -60% or greater than +120% of its value while reading the blank.
10.6.1.2 QCS (90-110%) and LFB (85-115%) samples should read within their proper range.
10.6.1.3 LFM (spike) samples should read within their analytical range (70-130%).
10.6.1.4 Duplicate samples should agree within 10% relative.
10.6.1.5 Standards when run should read their appropriate concentration.

11 Quality Assurance/Quality Control

11.1 See sec 10.6.1.

11.2 If the checks outlined in sec 10.6.1 do not meet specifications, rerun the set from which the bad data came. If continued problems exist refer to EPA method 200.8 for suggestive solutions.

12 Data Analysis

12.1 The instrument will calculate calibration curves for all elements and evaluate raw data counts against these calibrations. The results will be given in the appropriate units, typically μg/L. No data analysis beyond this is required.

13 Documentation

13.1 Document the tuning conditions and baseline information as outlined in sec 10.3.

14 Records

14.1 Records are kept, including all raw data, in the bottom orange file drawer in room

305. Records are periodically transferred to our storage facility for long term storage with the container marked with the appropriate disposal date.